

M.Sc.(Chem.) Semester - 4 (CBCS) Examination
Oct/Nov -2020 [NEW COURSE]
Modern Spectroscopy (Elective)

Time: 2:00 Hours

Marks: 56

Instructions:

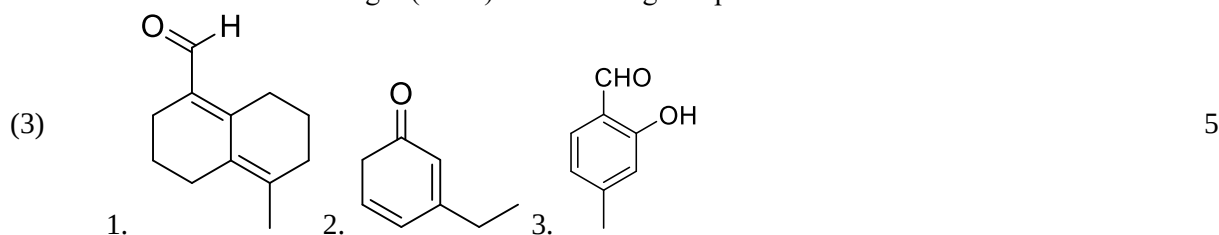
1. Figures to the right indicate marks.
2. There are five questions in the question paper.
3. Answer any four of the following questions.

Unit-1 [14 marks]Answer ALL questions**Q.1 (a) Answer the following.****4 Marks**

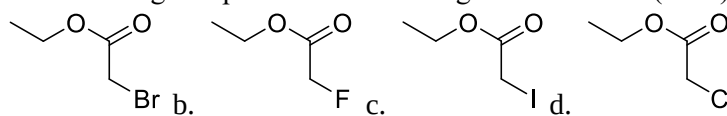
- (1) What is UV spectroscopy? Draw a schematic diagram of double beam UV Spectrophotometer. 4

Q.1 (b) Answer any two questions out of three.**10 Marks**

- (1) Explain different types of absorption and intensity shift observed in UV spectroscopy. 5
- (2) Discuss solvent effects in $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition in UV spectroscopy. 5
- Calculate the wavelength ($\lambda_{\max}$) for following compounds:

**Unit-2 [14 marks]**Answer ALL questions**Q.2 (a) Answer the following.****4 Marks**

1. Arrange the following compounds in decreasing order in their $\nu(\text{C=O})$ frequency:



2. What are overtone and combination bands in IR Spectroscopy?

Q.2 (b) Answer any two questions out of three.**10 Marks**

- (1) Discuss the advantages of FTIR spectroscopy. 5
- (2) Explain fundamental modes of vibration in IR spectroscopy. 5
- (3) Explain the instrument of IR spectroscopy with schematic diagram. 5

Unit-3 [14 marks]Answer ALL questions**Q.3 (a) Answer the following.****4 Marks**

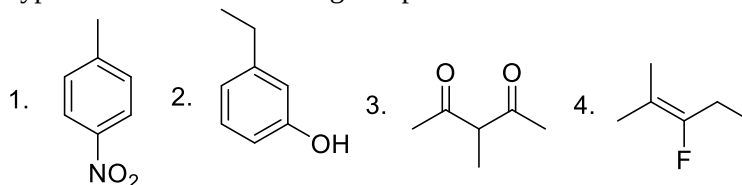
1. Define following terms:
- a) Base Peak
 - b) Parent Ion
 - c) Nitrogen rule
 - d) Steven's rule

- Q.3 (b)** Answer any two questions out of three. **10 Marks**
- (1) Discuss instrumentation of Mass spectroscopy with schematic diagram. 5
 - (2) Analyze the Mass Fragmentation patterns of Pentane. 5
 - (3) Discuss chemical ionization techniques in Mass spectroscopy. 5

Unit-4 [14 marks]
Answer **ALL** questions

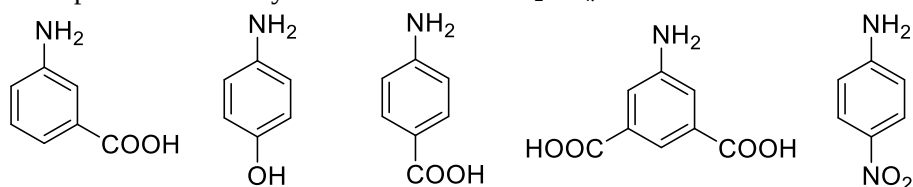
- Q.4 (a)** Answer the following. **4 Marks**

1. Identify the types of carbon in following compounds:

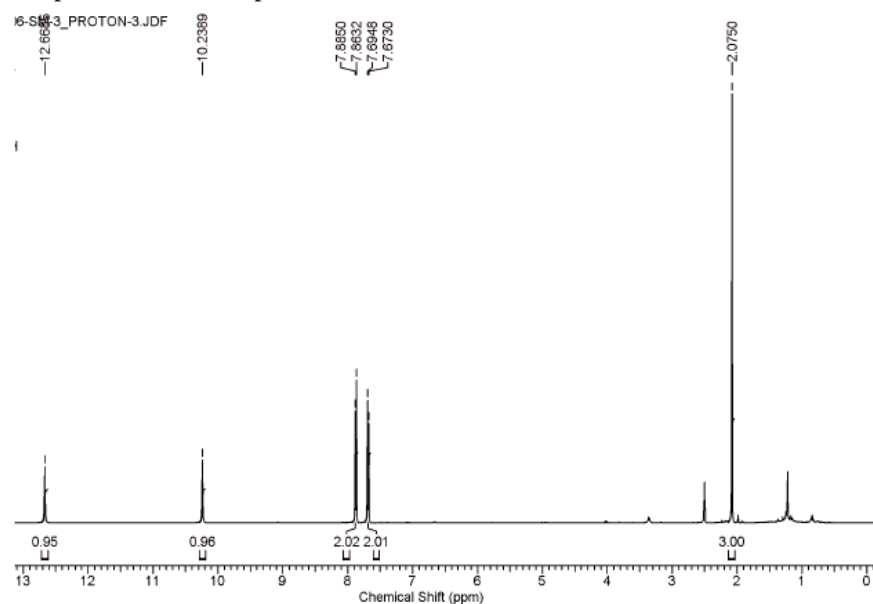


- Q.4 (b)** Answer any two questions out of three. **10 Marks**

- (1) Predict Spin-Spin splitting in 1-bromoethane and illustrate Pascal's triangle. Acetylation of following compounds were carried out with acetic anhydride in the presence of catalytic amount of Con. H_2SO_4 .



Among them one of the product 1H NMR spectrum is given below. Identify the product and interpret it.



- (2) 5

- (3) Which reference standard is used in NMR spectroscopy? And Why? 5

Unit-5 [14 marks]
Answer **ALL** questions

- Q.5 (a)** Answer the following. **4 Marks**

1. Give the Full form of following terms:
 - a) COSY
 - b) NOESY
 - c) HSQC
 - d) HMBC
2. Indicate the number of signals and multiplicity of Isopropyl benzene in off-resonance decoupled ^{13}C NMR spectra.

Q.5 (b) Answer any two questions out of three.**10 Marks**

- (1) Calculate the chemical shift value of carbon of following compounds: 5
1. 3-methylpentane 2. 1-hexene 3. p-cresol

An organic compound with MF: $C_6H_{10}O_4$ furnished the following spectral data:

UV: No significant absorption above 210 nm.

IR: 2950, 1765 and 1050 cm^{-1}

- (2) PMR: δ 1.5 (3H, d), 2.2 (6H, s) and 6.9 (1H, q) 5

CMR (Off-resonance decoupled): One singlet at δ 170, one doublet and two quartets

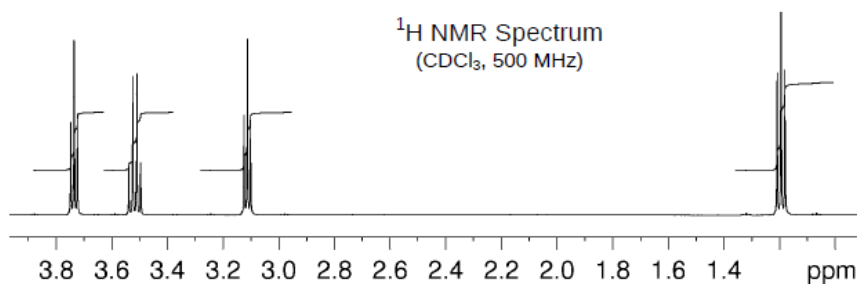
MS: Prominent peaks at m/e 146, 87 and 43.

Deduce the structure of the compound and explain the spectral data.

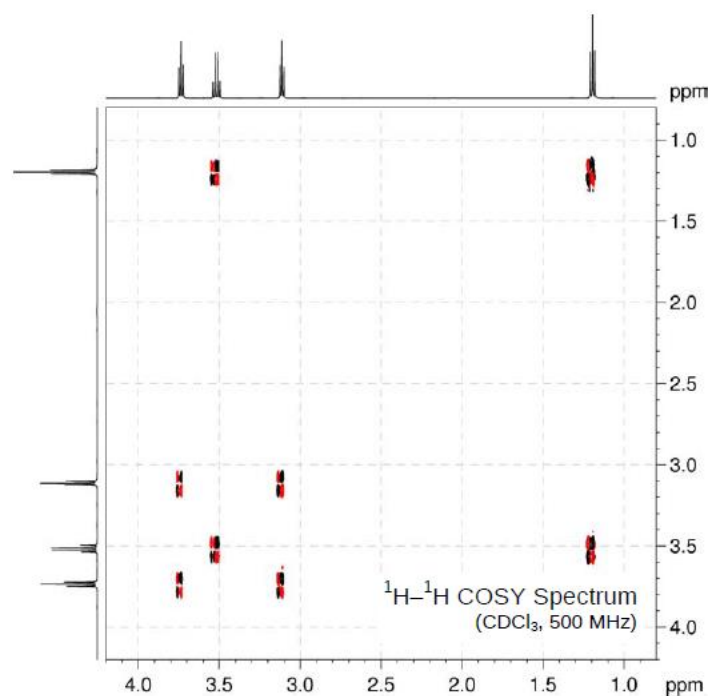
Deduce the structure of compound from the given spectral data and interpret correlation peak in 2D NMR and assign protons.

MF: $C_5H_9ClO_2$

PMR: δ 1.2 (3H, t), 3.1 (2H, t), 3.5 (2H, q), 3.7 (2H, t).

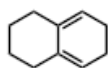
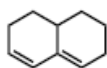


- (3) 5



UV Spectroscopy

Woodward Fieser Rules for Dienes

			
<i>s-trans</i>	homoannular (cisoid)	heteroannular (transoid)	
base values:	217 nm	253 nm	214 nm

Increments:

For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
For each alkyl group or Ring Residue	+ 5 nm
For each of the following groups:	
- OR	+ 6 nm
- O(C=O)R	+ 0 nm
- Cl	+ 6 nm
- Br	+ 6 nm
- SR	+ 30 nm
- NR ₂	+ 60 nm
- Ph	+ 60 nm

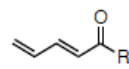
not affected by solvent

Where both types of cyclic dienes are present, the base with the longer λ_{max} is used.

UV Spectroscopy

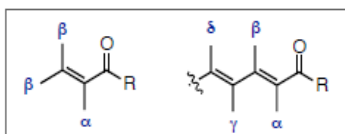
Woodward Fieser Rules for Enones

Solvent Correction	nm
H ₂ O	- 8
EtOH	0
CHCl ₃	+ 1
Dioxane	+ 5
Et ₂ O	+ 7
Hydrocarbon	- 11

				
acyclic enone	6-membered ring enone	5-membered ring enone	acyclic dienone	
base values:	215 nm	215 nm	202 nm	245 nm

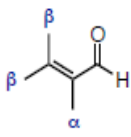
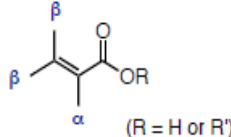
Increments:

	α	β	γ	δ and higher
For each additional conjugated double bond	+ 30 nm			
For each exocyclic double bond	+ 5 nm			
For each homodiene component	+ 39 nm			
For each alkyl group	+ 10 nm	+ 12 nm	+ 18 nm	+ 18 nm
For each of the following groups:				
- OH	+ 35 nm	+ 30 nm		+ 50 nm
- OR	+ 35 nm	+ 30 nm	+ 17 nm	+ 31 nm
- O(C=O)R	+ 6 nm	+ 6 nm		+ 6 nm
- Cl	+ 15 nm	+ 12 nm		
- Br	+ 25 nm	+ 30 nm		
- SR	+ 30 nm	+ 85 nm		
- NR ₂	+ 60 nm	+ 95 nm		



UV Spectroscopy

Woodward Fieser Rules for Other Conjugated Carbonyls

	
aldehydes	carboxylic acid or ester

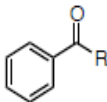
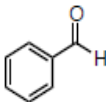
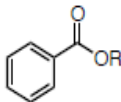
Base Values

unsubstituted aldehyde or ester	208 nm	195 nm
with α or β alkyl groups	220 nm	208 nm
with α,β or β,β alkyl groups	230 nm	217 nm
with α,β,β alkyl groups	242 nm	225 nm
for an exocyclic α,β double bond		+ 5 nm
for an endocyclic α,β double bond in a 5- or 7-membered ring		+ 5 nm

as for enones, solvent correction is also relevant

UV Spectroscopy

Woodward Fieser Rules for Benzoyl Derivatives

			
	aryl ketones (R = alkyl)	benzaldehydes	benzoic acids and esters
base values:	246 nm	250 nm	230 nm

Increments:	ortho	meta	para
For each alkyl group or RR	+ 3 nm	+ 3 nm	+ 10 nm for RR + 7 nm
For each OH or OR (R = alkyl)	+ 7 nm	+ 7 nm	+ 25 nm
For each O ⁻	+ 11 nm	+ 20 nm	+ 78 nm
For each of the following groups:			
- Cl	+ 0 nm	+ 0 nm	+ 10 nm
- Br	+ 2 nm	+ 2 nm	+ 15 nm
- NH ₂	+ 13 nm	+ 13 nm	+ 58 nm
- NH(C=O)CH ₃	+ 20 nm	+ 20 nm	+ 45 nm
- NHCH ₃			+ 73 nm
- N(CH ₃) ₂	+ 20 nm	+ 20 nm	+ 85 nm

Standard Data Sheet for IR spectroscopy

CHARACTERISTIC INFRARED ABSORPTION BANDS OF FUNCTIONAL GROUPS

Class of Compounds	Absorption, cm ⁻¹	Intensity	Assignment	Class of Compounds	Absorption, cm ⁻¹	Intensity	Assignment
Alkanes and Alkyls	2850-3000 1450-1470 1370-1390 1365 + 1395 (two bands) 715-725	s s m m w	C-H stretch C-H bend CH ₃ C-H bend -CH(CH ₃) ₂ or -(CH ₃) ₃ bend -(CH ₂) _n bend	Carboxylic Acids	2500-3500 1710-1715 1680-1710	s, broad s, broad s	O-H stretch C=O stretch C=O stretch
Alkenes	3020-3140 1640-1670 910 + 990 (two bands)	w-m vw-m m + s	=C-H stretch C=C stretch =C-H bend	Esters	aliphatic 1160-1210 acetates ~1240 aromatic 1250-1310	s-vs s s	O=C-O-C stretch C=O stretch C=O stretch
RCH=CH₂	885-895 665-730 960-980 790-840	s m-s, broad s s	=C-H bend =C-H bend =C-H bend =C-H bend	Acyl Chlorides	1735-1750 1715-1730 1760-1790	s s s	C=O stretch C=O stretch C=O stretch
RR'C=CH₂				Aldehydes	1785-1815 1770-1800	s s	C=O stretch C=O stretch
cis-RCH=CHR'				Anhydrides			
trans-RCH=CHR'				R-C(O)-O-C(O)-R	~1750 + ~1815	s,s	C=O symmetric
RCH=CR'R''				Ar-C(O)-O-C(O)-Ar	~1720 + ~1775 (both two bands)	s,s	& asym. stretch
Alkynes				Nitriles			
R-C≡C-H	3265-3335 2100-2140 610-700	s, sharp m s, broad	≡C-H stretch C≡C stretch ≡C-H bend	R-C≡N	2240-2260	m-s	C≡N stretch
R-C≡C-R'	2190-2260	vw-w	C≡C stretch	C≡C-N or Ar-C≡N	2220-2240	s	C≡N stretch
Alkyl halides				Amines			
R-F	1000-1350	vs	C-F stretch	R-NH₂	~3400 + ~3500 (two bands) 1580-1650	w w-m	N-H symmetric & asym. stretch N-H bend
R-Cl	750-850	s	C-Cl stretch	RR'N-H	3310-3335	w	N-H stretch
R-Br	500-680	s	C-Br stretch	Amides			
R-I	200-500	s	C-I stretch	R-C(O)-NH₂	3200-3400 and 3400-3500 (two bands) 1650-1690	w-m s, broad	N-H symmetric & asym. stretch C=O stretch
Alcohols	3300-3400 1035-1050 1050-1085	s, broad m-s m-s	O-H stretch C-O stretch C-O stretch	R-C(O)-NH-R	1590-1655 3400-3500 1640-1690	m-s w-m s, broad	N-H bend N-H stretch C=O stretch
R-CH₂-OH (1°) or C=C-CH(R)-OH	1085-1125	m-s	C-O stretch	R-C(O)-NR'R''	1510-1560 1630-1680	m-s m-s	N-H bend C=O stretch
RR'CH-OH (2°) or C=C-CRR'-OH	1125-1205	m-s	C-O stretch	Nitro Compounds			
RR'R''C-OH (3°)	1180-1260	m-s	C-O stretch	R-NO₂	~1550 and ~1370 ~1525 and ~1335 (both two bands)	s s s	N-O symmetric & asym. stretch N-O symmetric & asym. stretch
Ethers				Aromatic Compounds	3010-3100 1450-1600 (two to four bands)	m m-s sharp	Ar C-H stretch ring C=C stretch
R-O-R'	1085-1150	s	C-O-C stretch	monosubstituted	730-770 and 690-710 (two bands)	s s	C-H bend C-H bend
Ar-O-R	1020-1075 and 1200-1275 (two band)	m-s	=C-O-C sym. & asym. stretch	o-disubstituted	735-770	s	C-H bend
Aldehydes	2700-2725 1720-1740 1685-1710	m s s	H-C=O stretch C=O stretch C=O stretch	m-disubstituted	750-810 and 690-710	s s	C-H bend C-H bend
C=C-CH=O or Ar-CH=O				p-disubstituted	810-840	s	C-H bend
Ketones							
RR'C=O	1710-1720	s	C=O stretch				
C=C-C(O)-R	1665-1685	s	C=O stretch				
Ar-C(O)-R	1675-1695	s	C=O stretch				
four member cyclic	1770-1780	s	C=O stretch				
five member cyclic	1740-1755	s	C=O stretch				
six member cyclic	1710-1720	s	C=O stretch				

Intensity abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Standard chemical shift value (ppm from TMS)

¹³C chemical shifts for some linear and branched-chain alkanes

Alkane	C-1	C-2	C-3	C-4	C-5
Methane	-2.5				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2	13.4	
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Isobutene	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Neopentane	31.7	28.1			
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH ₃)	

Olefinic carbons	
Substituent carbon C	Correction
α	+10.6
β	+7.2
γ	-1.5
α'	-7.9
B'	-1.8
γ'	-1.5
z (cis)	-1.1

Increments* (ppm) for substituents Y on alkanes

Substituent Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+9	+6	+10	+8	-2
HC=CH ₂	+20		+6		-0.5
C≡CH	+4.5		+5.5	+2	-3.5
COOH	+21	+16	+3	+2	-2
COO ⁻	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCI	+33	+28		+2	
CONH ₂	+22		+2.5		-0.5
COR	+30	+24	+1	+1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+9	+7	-2
OH	+48	+41	+10	+8	-5
OR	+58	+51	+8	+5	-4
OCOR	+51	+45	+6	+5	-3
NH ₂	+29	+24	+11	+10	-5
NH ₃ ⁺	+26	+24	+8	+6	-5
NHR	+37	+31	+8	+6	-4
NR ₂	+42		+6		-3
NH ₃ ⁺	+31		+5		-7
NO ₂	+63	+57	+4	+4	
CN	+4	+1	+3	+3	-3
SH	+11	+11	+12	+11	-4
SR	+20		+7		-3
F	+68	+63	+9	+6	-4
Cl	+31	+32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	-6	+4	+11	+12	-1

Increments in the shifts of the aromatic carbon atoms of monosubstituted benzenes (ppm from benzene at 128.5 ppm)

Substituent	C-1	C-2 (<i>ortho</i>)	C-3 (<i>meta</i>)	C-4 (<i>para</i>)
H	0.0	0.0	0.0	0.0
CH ₃	+9.3	+0.7	-0.1	-2.9
CH ₃ CH ₂	+15.6	-0.5	0.0	-2.6
CH(CH ₃) ₂	+20.1	-2.0	0.0	-2.5
HC=CH ₂	+9.1	-2.4	+0.2	-0.5
C ₆ H ₅	+12.1	-1.8	-0.1	-1.6
F	+35.1	-14.3	+0.9	-4.5
Cl	+6.4	+0.2	+1.0	-2.0
Br	-5.4	+3.4	+2.2	-1.0
I	-32.2	+9.9	+2.6	-7.3
OH	+26.6	-12.7	+1.6	-7.3
OCH ₃	+31.4	-14.4	+1.0	-7.7
CHO	+8.2	+1.2	+0.6	+5.8
COCH ₃	+7.8	-0.4	-0.4	+2.8
COOH	+2.9	+1.3	+0.4	+4.3
CN	-16.0	+3.6	+0.6	+4.3
NO ₂	+19.6	-5.3	+0.9	+6.0
NH ₂	+19.2	-12.4	+1.3	-9.5
NHCOCH ₃	+11.1	-9.9	+0.2	-5.6
COOCH ₃	+2.0	+1.2	-0.1	+4.8
